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• Brons, Cornelius Hendrick
Washington, New Jersey 07882 (US)

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(74) Representative:
Fletcher Watts, Susan Jane et al
ESSO Engineering (Europe) Ltd.,
Patents & Licences,
Mailpoint 70,
Esso House,
Ermyn Way
Leatherhead, Surrey KT22 8XE (GB)

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(71) Applicant:
ExxonMobil Research and Engineering
Company (Delaware Corp)
Florham Park, New Jersey 07932-0390 (US)

(72) Inventors:
• Varadaraj, Ramesh
Flemington, New Jersey 08822 (US)

(54) Urea-surfactant clathrates

(57) The present invention provides novel adducts of urea with a surfactant which is either (i) a non-ionic surfactant selected from the group consisting of a diethylene glycol monoalkyl ether, a phosphate ester of polyoxyethylene glycol monoalkyl ether, N-di(polyoxyethylene glycol monoxide)propanolamine undecyl ether, a sorbitan mono-oleate, a polyoxyethylene glycol mono(sorbitan mono-oleate)ether and their cyclic ethers, a sorbitan dodecanate, or, (ii) an ammonium salicylate salt of N-di(polyoxyethylene glycol monoxide)propanolamine undecyl ether. These adducts are suitable for use in bioremediation of hydrocarbon contaminated soils and water.

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Description

[0001] This invention relates to urea-surfactant clathrates suitable for use in enhancing the microbial degradation of hydrocarbon contaminated soils and water.

[0002] As is well-known there are several microbial species found in soil and water that are capable of assimilating petroleum hydrocarbons. Unfortunately, the rate of microbial assimilation of petroleum hydrocarbons is relatively slow. It is necessary therefore to stimulate the microbial assimilation of petroleum hydrocarbons if bioremediation is to be utilized in removing such pollutants from soils and water.

[0003] In general, the rate and extent of microbial utilization of petroleum hydrocarbons is limited by the concentration of microbial nutrients and microflora available at the hydrocarbon water interface. Therefore, microbial nutrients, especially nitrogen containing nutrients like urea, have been added to contaminated soil or water as a method for enhancing the biodegradation of the petroleum contaminants. Because these nitrogen containing microbial nutrients are generally water soluble, and because the petroleum hydrocarbons are hydrophobic several different techniques have been used for delivering the nutrients to the hydrocarbon-water interface. For example, one technique employed is to coat the nutrients with a material such as petrolatum in an attempt to keep the nutrient at the hydrocarbon water interface. Another technique that has been employed is to deliver the nutrients in an aqueous solution along with a surfactant which aids in delivering the microbial nutrients to the hydrocarbon-water interface.

[0004] There are, of course, many other facets to the treatment of contaminated soils and water and many researchers have worked towards discovering more successful processes for improving biodegradation of contaminated soils and water.

[0005] In the prior art such as e.g. GB-A-697315 and GB-A-747877 several adducts of urea with non-ionic surfactants such as e.g. polyoxyethylene glycals, their monoethers ethers and their ester-esters are described. However, no use is attributed to these, especially in respect of their ability to biodegrade hydrocarbons.

[0006] The present invention also provides compositions containing such novel compounds suitable for use in stimulating the propagation of naturally occurring, hydrocarbon assimilating, microflora to enhance the bioremediation of hydrocarbon contaminated soils and water.

[0007] Accordingly, the present invention provides an adduct of urea with a surfactant which is either (i) a non-ionic surfactant selected from the group consisting of a diethylene glycol monoalkyl ether, a phosphate ester of a polyoxyethylene glycol monoalkyl ether, N-di(polyoxyethylene glycol monoxide)propanolamine undecyl ether, a sorbitan monooleate, a sorbitan dodecanoate, polyoxyethylene glycol mono(sorbitan mono-oleate)ether and their cyclic ethers, or, (ii) an ammonium salicylate salt of N-di(polyoxyethylene glycol monoxide)propanolamine undecyl ether.

[0008] In another embodiment of the present invention, there is provided a composition suitable for enhancing the bioremediation of contaminated soils and water which comprises at least one adduct of urea with a surfactant, preferably in combination with a phosphorus source.

[0009] Novel compounds of the present invention are adducts or inclusion complexes of urea with a surfactant, in which urea in the "host" and the surfactant is the "guest". In general, weight ratio of urea to surfactant in the adduct will be in the range from 98:2 to 75:25, and preferably in the range from 80:20 to 76:24.

[0010] The surfactant suitable for forming the novel compounds of the present invention are those surfactants which are capable of forming clathrates with urea. These may be non-ionic or ionic salts. Non-limiting examples of non-ionic surfactants are alkyl ethoxylated phosphates, alkyl ethoxylated-amines, alkyl ethoxylated sugars and alkyl ethoxylated polyhydric alcohols and their cyclic ethers, such as sorbitol and sorbitan, in which the alkyl groups will have from about 8 to 22 carbon atoms, or salts such as alkyl ethoxylated ammonium salts and in each of which the ethylene oxide groups will range from about 2 to 50 and may be monodispersed or polydispersed.

[0011] The adducts of the present invention can be readily synthesized by co-crystallizing urea and the surfactant from an appropriate solvent. Typical solvents in preparing the urea-surfactant adducts include alcohols such as methanol and mixed solvents such as methanol/isopropyl alcohol in volume ratios of about 80 to 20. Typically, the urea and surfactant are dissolved in the solvent at elevated temperatures, e.g., at about 50°C, and thereafter the solvent is allowed to evaporate slowly with the concomittant formation of crystals of the adduct.

[0012] Not wishing to be bound by any theory or mechanism it is believed that the novel surfact-urea adducts of the present invention when contacted with water disassociate in such a fashion that at least some of the urea molecules stay associated with the head group of the surfactant thereby enhancing the delivery of the urea to the hydrocarbon-water interface where it is most needed for stimulating microbial growth and assimilation of hydrocarbon contaminants.

[0013] In any event, compositions for enhancing the biodegradation of hydrocarbon contaminated soils and water comprise at least one adduct of urea and a non-ionic surfactant. Preferably, the surfactant will be selected from those surfactants described above. Preferably the urea-surfactant adduct is combined with a phosphorus source. It is particularly preferred, however, that the urea surfactant clathrate be combined with the phosphorus source or other microbial nutrients to obtain a composition having a N:P ratio in the range of 10:2 to 10:0.5 and preferably about in the range 10:1. Such other microbial nutrients that can be added to the clathrate include ammonium hydrogen phosphate, sodium

phosphate, and the like. In some instances, more than one adduct of urea and non-ionic surfactant can be successfully combined.

[0014] In addition to the urea surfactant adduct and phosphorus source, optionally, the compositions may include other components such as salicylates to stimulate aromatic degradation and micro nutrients typically used in bioremediation processes.

[0015] Non-limiting examples of various compositions are given in Table 1 which follows. In each of the formulations the weight ratio of urea to surfactant was 83:17.

TABLE 1

| Formulation | Urea Surfactant/Wt. % | Phosphorus Source/Wt. % |
|-------------|--|--|
| 1 | Urea-Oleyl-2-ethoxylate/44% | NH ₄ H ₂ PO ₄ /12% |
| | Urea-trilaurethphosphate/44% | |
| 2 | Urea-tetradecylammonium salicylate 44% | NH ₄ H ₂ PO ₄ /12% |
| | Urea-trilaurethphosphate/44% | |
| 3 | Urea-trilaureth phosphate/83.4% | NH ₄ H ₂ PO ₄ /10.6% Sodium Salicylate/6% |

[0016] In treating contaminated soil and water in accordance with the present invention, the urea surfactant composition is applied to the soil or water by broadcasting in an amount sufficient to enhance the rate of biodegradation of the contaminated soil and water. The amount applied can vary broadly and typically will depend upon the weight percent of hydrocarbon contaminant on the soil or water. Preferably, the amount of the urea-surfactant formulation will be applied in an amount sufficient to provide a C:N:P ratio of from about 100:10:1 to about 100:1:0.1.

[0017] When treating contaminated soil with compositions of the present invention, it is generally preferred or attempted to maintain the moisture content of the hydrocarbon contaminated soil at from about 10 wt.% to 35 wt.%.

[0018] The following examples will more fully illustrate the invention.

Examples 1-10

[0019] These examples demonstrate the preparation of the novel urea non-ionic surfactant adducts of the present invention.

[0020] To 20 gm. of methanol was added 5 gm. of urea and 1 gm. of the surfactant shown in Table 2. The mixture was heated until the urea and surfactant both dissolved. After cooling to room temperature, the solvent was allowed to evaporate very slowly and the urea-surfactant clathrate crystals formed were separated by filtration, washed with cold methanol and dried. The weight ratio of urea to surfactant for each composition prepared is given in Table 2.

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TABLE 2

| <u>Example</u> | <u>Surfactant Commercial Name</u> | <u>Nominal Formula</u> | <u>Wt.% Urea/Surfactant</u> |
|----------------|--|---|-----------------------------|
| 1 | Brij-92 ¹ | C ₁₈ H ₃₅ -(OCH ₂ CH ₂) ₂ -OH | 83/17 |
| 2 | Trilaureth Phosphate | (C ₁₂ H ₂₅ -(O-CH ₂ CH ₂) ₄ -O) ₃ -P=O | 83/17 |
| 3 | Tween-80 ² | C ₁₈ H ₃₅ -CO ₂ -Sorbitan-(OCH ₂ CH ₂) ₁₀ -OH | 83/17 |
| 4 | Span-80 ³ | C ₁₈ H ₃₅ -CO ₂ -Sorbitan | 83/17 |
| 5 | Span-20 | C ₁₂ H ₂₅ -CO ₂ -Sorbitan | 83/17 |
| 6 | E-14-5 Ethoxylated Amine ⁴ | $\begin{array}{c} (\text{OCH}_2\text{CH}_2)_y\text{-OH} \\ \\ \text{C}_{11}\text{H}_{23}\text{-O-(CH}_2)_3\text{-N} \\ \\ x + y = 5 \end{array}$ | 83/17 |
| 7 | E-14-5 Ethoxylated Ammonium Salicylate | $\begin{array}{c} (\text{OCH}_2\text{CH}_2)_y\text{-OH} \\ \\ \text{C}_{11}\text{H}_{23}\text{-O-(CH}_2)_3\text{-N-Salicylic Acid} \\ \\ (\text{OCH}_2\text{CH}_2)_x\text{-OH} \\ \\ x + y = 5 \end{array}$ | 83/17 |

1. Brij-92 is the trade name for an ethoxylated alcohol sold by ICI America's, Inc., Wilmington, DE.

2. Tween-80 is the trade name of an ethoxylated Sorbitan ester sold by ICI American's Inc., Wilmington, DE.

10 3. Span 80 and Span 20 are trade names of Sorbitan esters sold by ICI Americas Inc., Wilmington, DE.

15 4. E-14-5 ethoxylated amine is the trade name of an ethoxylated amine sold by Exxon Chemical Company, Houston, TX.

20 Examples 8 and 9

[0021] In these two examples, Formulations 1 and 2 of Table 1 were prepared and tested in the biodegradation of refinery soil. The N:P ratio of the formulations were 10:1.

25 [0022] The tests were conducted as follows. A refinery soil having weathered hydrocarbon contaminants was used which had approximately one weight percent contaminant as determined by EPA Method 418.1. To three separate polypropylene pans, 12 inches long, by 8 inches wide and 3 inches deep, 2,000 gms of the hydrocarbon contained contaminated soil were added. Two of the pans were treated by uniformly broadcasting the urea-surfactant formulation onto the soil surface to provide a C:N:P of 100:10:1. The soil in the pans were watered and hand-tilled weekly. The amount of 30 water applied was sufficient to provide a moisture content of about 17 wt.%. After 8 weeks, the percent petroleum hydrocarbon biodegraded was determined for each of the samples using the EPA Method 418.1 with the following modifications.

35 1. The soil sample size was increased to 30 grams.
 2. The acidification step specified in the test was eliminated.
 3. The drying agent used was magnesium sulfate.
 4. The amount of drying agent required by the test was increased to assure effective drying.
 5. A four hour time period for soxhlet extraction was employed.
 6. The amount of silica gel used in the final filtration step was increased.

40 [0023] The microbial population was determined on the soil samples 2 weeks after treatment. The standard most probable number (MPN) microbiology method was employed and a two week incubation period was allowed. The results of these tests are shown in Table 3.

45 [0024] Additionally, one pan, a control pan, containing untreated soil was watered, hand tilled and subjected to the same tests outlined above. In this instance the control is labelled Comparative Example 1 and the results for it are also given in Table 3.

TABLE 3

| Example | Formulation | % Hydrocarbon Biodegraded In 8 Weeks | Microbial Population MPN Heterotrophs |
|---------------|-------------|--------------------------------------|---------------------------------------|
| 8 | 1 | 22 | 7.5 E+04 |
| 9 | 2 | 20 | 8.6 E+04 |
| Comparative 1 | - | 2 | 1.7 E + 02 |

[0025] The formulations 1-3 listed in Table 1 were also tested using a refinery landfarm soil sludge. In these tests,

three kilograms of a refinery landfarm sludge sieved to contain soil particles less than 2mm in size was added to an oily refinery sludge so that the effective hydrocarbon contaminant on the soil was 2.5 wt.%.

[0026] Five polypropylene pans with the same dimensions as outlined in Examples 8 and 9, each containing 3 kilograms of soil were set up and treated with the formulations as shown in the Table 4. To three of the pans the solid formulations were broadcast onto the surface with periodic tilling and mixing of the soil sludge.

[0027] The fourth pan was treated with granular urea and sodium phosphate (combined to provide a C:N:P ratio of 100:10:1). This is labelled Comparative Example 2. In Table 4, the fifth pan was untreated but otherwise watered, band tilled and tested. The result of the control pan labelled Comparative Example 3 in Table 4.

[0028] As indicated, all the pans were watered and tilled three times per week. The percent hydrocarbon that biodegraded was determined by the modified EPA 418.1 Test Method outlined above for each pan every two weeks for 9 weeks. From the time versus percent biodegraded data pseudo first order rate constants were determined for each treatment. These results are presented in Table 4.

TABLE 4

| Example | Formulation | % Hydrocarbon Degraded In 9 Weeks | Pseudo First Order Rate Constant (1/Days) |
|---------------|-------------|-----------------------------------|---|
| 10 | 1 | 18 | 1.14 E-03 |
| 11 | 2 | 17 | 2.33 E-03 |
| 12 | 3 | 31 | 4.21 E-03 |
| Comparative 2 | - | 7 | 4.21 E - 05 |
| Comparative 3 | - | 0 | - |

It should be readily appreciated that the foregoing Examples are not intended to be limiting but merely intended to be illustrative of the mechanisms and materials pertaining to the invention.

Claims

1. An adduct of urea with a surfactant which is either (i) a non-ionic surfactant selected from the group consisting of a diethylene glycol monoalkyl ether, a phosphate ester of polyoxyethylene glycol monoalkyl ether, N-di(polyoxyethylene glycol monoxide)propanolamine undecyl ether, a sorbitan monooleate, a polyoxyethylene glycol mono(sorbitan mono-oletate)ether and their cyclic ethers, a sorbitan dodecanoate, or, (ii) an ammonium salicylate salt of N-di(polyoxyethyleneglycol monoxide)propanolamine undecyl ether.
2. A adduct according to Claim 1 wherein the alkyl grouping in surfactant (i) has 8 to 22 carbon atoms.
3. An adduct according to Claim 1 or 2 wherein each of the surfactants in (i) and (ii) has from 2 to 50 ethylene oxide groups.
4. An adduct according to any one of the preceding Claims wherein the weight ratio of urea to the surfactants in (i) or (ii) is the range from about 98:2 to about 75:25.
5. Adducts according to any one of the preceding Claims wherein said adducts comprise two adducts of urea and the surfactants in (i) and/or (ii).

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(71) Applicant:
ExxonMobil Research and Engineering
Company (Delaware Corp)
Florham Park, New Jersey 07932-0390 (US)

(72) Inventors:

- Varadaraj, Ramesh
Flemington, New Jersey 08822 (US)
- Brons, Cornelius Hendrick
Washington, New Jersey 07882 (US)

(74) Representative:

Fletcher Watts, Susan Jane et al
ESSO Engineering (Europe) Ltd.,
Patents & Licences,
Mailpoint 70,
Esso House,
Ermyn Way
Leatherhead, Surrey KT22 8XE (GB)

(54) Urea-surfactant clathrates

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EUROPEAN SEARCH REPORT

Application Number
EP 00102234.2

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | |
|---|--|--|--|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int. Cl. 7) |
| X | GB 748877 A (BRITISH PETROLEUM COMPANY LIMITED) 16 May 1956, page 1, lines 37-63, page 2, lines 78-81, 121-123, claims 1,8. -- | 1-4 | C02F1/00 C02F3/24 C07C273/00 |
| X | GB 697315 A (ANGLO-IRANIAN OIL COMPANY LIMITED) 23 September 1953, page 2, lines 69-74, claims 1,11. ---- | 1-3 | |
| | | | TECHNICAL FIELDS SEARCHED (Int. Cl. 7) |
| | | | C02F C07C C11D |
| <p>The present search report has been drawn up for all claims</p> | | | |
| Place of search VIENNA | Date of completion of the search 05-07-2000 | Examiner KOLLER | |
| CATEGORY OF CITED DOCUMENTS | | E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons &: member of the same patent family, corresponding document | |
| X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention | | | |

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO. EP 00102234.2**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned search report. The members are as contained in the EPIDOS INPADOC file on 10.07.2000. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|----------------------------|---------------------|
| GB A 748877a1 | | none | |
| GB A 697315a1 | | none | |

For more details about this annex see Official Journal of the European Patent Office, No. 12/82.

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